Electronic Structure of Single Wall Carbon Nanotubes Studied by Resonant Inelastic X-Ray Scattering

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Carbon nanotubes have in recent years attracted increasing interest as a new modification of carbon, related to the fullerenes and graphite. Especially for single wall carbon nanotubes (SWNTs) interesting electronic properties have been predicted early on. [1] For these nanotubes, the electronic structure strongly depends on the chirality vector defining the type of nanotube: *(n, n)* tubes ("armchair" type) are predicted to be metallic, while *(n, m)* tubes with $n \neq m$ are wide-gap or narrow-gap semiconductors, depending on the particular m and n. If $2n+m$ or $n+2m$ is an integer multiple of 3, the SWNT is predicted to be a narrow-gap semiconductor with good room temperature conductivity.

This behaviour can be understood in a straightforward quantum confinement approach starting from the bandstructure for a single graphene sheet. Due to the boundary conditions for electron wavevectors, only a subset of states ('slice') in the graphene BZ will be allowed in a SWNT. [7]

Just as in graphite or a graphene sheet, where the metallicity stems from degenerate states at the *K*-point in the BZ (Fig. 1), the nanotube will only be metallic if the *K*-point is contained in the set of allowed states. For simple geometric reasons, this is always the case for *(n, n)* nanotubes, as shown in Fig. 2. Further BZ geometry reveals that for all other nanotubes, a slice can only cut through *K* if $2n+m$ or $n+2m$ is an integer multiple of 3. In nanotubes, however, the degenerate point is slightly shifted away from the *K*-point. As a result, the degenerate point can only be reached exactly in *(n, n)* SWNTs, for *(m, n-m)* nanotubes the calculations show a gap of at least a few meV ("narrow-gap SWNTs"). [1]

For SWNTs to exhibit good conductivity at room temperature, filled and empty states close to E_F are necessary. As outlined above, these states are derived from states in the immediate these states show up at different points along $\overline{\Gamma X}$ in the bandstructure for a vicinity of the *K*-point in graphite. Depending on the orientation and number of ***k***-space slices, nanotube (even at *Γ*).

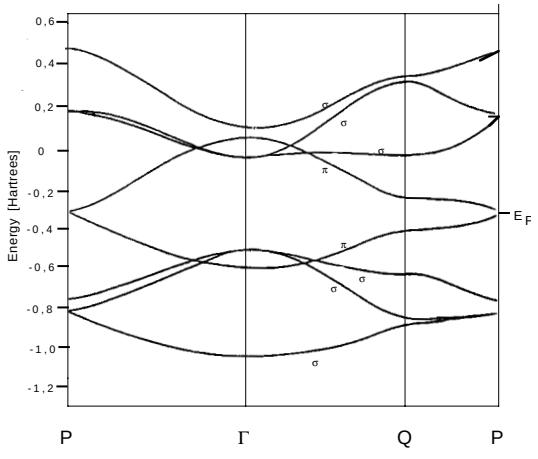

Fig. 1: Band structure of a single graphene sheet. Adapted from Ref. [13]. Please note that E_F is located at about –9 eV (–0.33 Hartrees) on the energy scale.

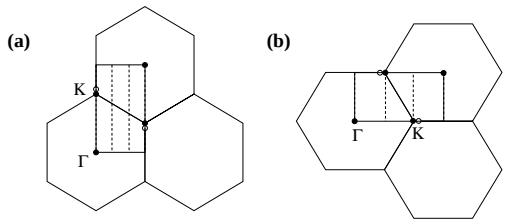

Fig. 2: Illustration of the slices through the 2-dimensional BZ of Graphene in order to find the SWNT states fulfilling the periodic boundary condition. *Γ*- and *K*-point are indicated by full circles, the degenerate point close to *K* is marked by an open circle. The rectangular Brillouin zones of the SWNTs and the slices (dashed lines) are shown. (a) SWNT of *(n, n)* "armchair" type. A slice will always cut through the degenerate point. (b) SWNT of *(n, 0)* "zigzag" type. A slice can only cut through the *K*-point (and hence in the immediate vicinity of the degenerate point) if the BZ is cut into an integer multiple of 3 equal parts. Adapted from Ref. [1].

Only recently has it become possible to synthesize larger amounts of SWNTs with high purity and narrow distributions in the tube diameter [3], making more detailed experimental studies of the electronic structure as a function of tube size and/or chirality possible. Of particular interest is experimental evidence for the existence of SWNTs with electronic states close to E_F, as their presence in samples prepared in various ways has been a matter of debate. As we will demonstrate below, our results indicate that such SWNTs with high room temperature conductivity are present in our sample and that their electronic structure can be selectively probed.

We report on studies of SWNTs using soft x-ray emission (SXE) and resonant inelastic soft x-ray scattering (RIXS). In SXE, the fluorescent decay of a previously created core hole is monitored. In particular, transitions from occupied valence states to the unoccupied core state yield information on the density of states of the system under investigation. As a dipole transition to a localized core orbital is involved, only states with the appropriate symmetry character that are localized in the vicinity of the core orbital will contribute to the spectra. Hence, the spectra measure the local partial density of occupied states (occupied LPDOS). In RIXS, a closely related technique, additional information can be obtained on the wavevector of occupied electronic states, similar to angle resolved photoemission. [4, 5] Here, a core vacancy is created by selectively promoting the core electron into unoccupied states of a chosen energy. Under certain conditions, valence band electrons with the same wavevector as the excited electron will then contribute predominantly in the consecutive SXE process. [6] As a result, parts of the BZ can be probed selectively by variation of the excitation energy. Simply put, RIXS enhances those occupied states in the spectra that have the same crystal momentum as the excited electron.

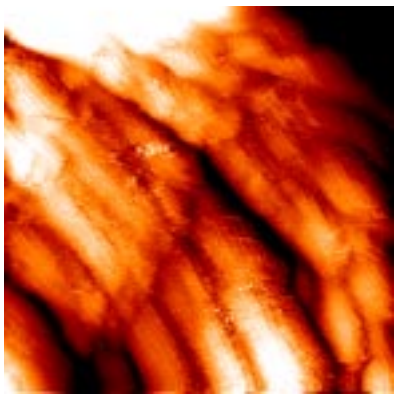

Fig. 3: STM image from a free-standing sheet of buckypaper. The image size is 250 nm x 250 nm. The organization of individual SWNTs into microbundles and ropes can be seen. Individual SWNTs as typically 1.2 nm in diameter and show up as fine stripes. [8]

We have studied SWNTs in a disk of purified "buckypaper" [7], prepared as described by Rinzler *et al.* [3] The material is a paper-like felt, where SWNTs form microbundles which in turn form ropes. These ropes are randomly woven to form the felt. In Fig. 3 we present a scanning tunneling microscope image recorded on the intact buckypaper showing the organization of individual SWNTs into microbundles and ropes. [8] TEM analysis shows a narrow diameter distribution for the individual SWNTs strongly peaked at 1.2 nm. [3]

RIXS was performed at beamline 7.011 of the Advanced Light Source, Berkeley, using a grazing incidence Rowland spectrometer, employing a 5m grating with 400 lines/mm in first order and a 20 μm entrance slit. In this configuration, the experimental resolution in the emission channel was determined to be about 0.7 eV. The resolution for RIXS excitation was 0.4 eV. SXE was excited by 3 keV electrons using a 10 μm entrance slit but otherwise the same setup as for the RIXS spectra. Both techniques are bulk sensitive with an information depth of about 0.1 μm.

The SXE spectra (not shown, see Ref. [7]) indicate that the valence band electronic structure of our sample is similar yet distinctly different from both graphite and C_{60} and cannot be interpreted as a superposition of the spectra from those materials.

For a more detailed analysis of the electronic states we now discuss the RIXS spectra. The excitation energies for the RIXS spectra are shown together with the absorption spectra of SWNTs, C_{60} and graphite in Fig. 4. For the raw RIXS data see Ref. [7]. Here, we present in Fig. 5 the RIXS spectra after subtraction of (1) the elastic peak due to diffuse reflection/ recombination and (2) the ***k***-unselective ("incoherent") contributions. [14, 15]

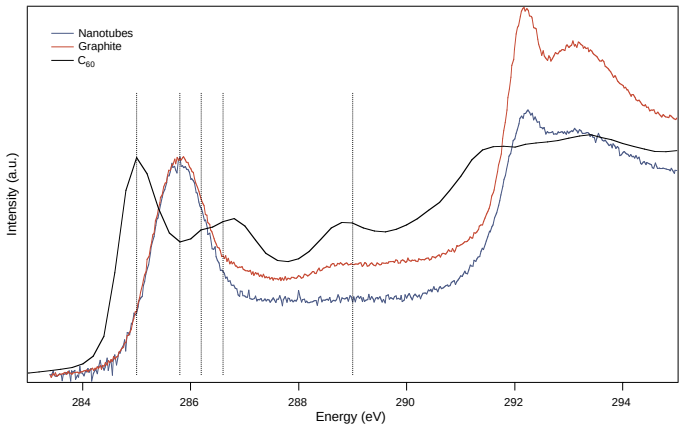

Fig. 4: Soft x-ray absorption of single wall carbon nanotubes (solid line), C_{60} (dashed line) and non-oriented graphite (dotted line). Vertical lines indicate excitation energies for RIXS spectra.

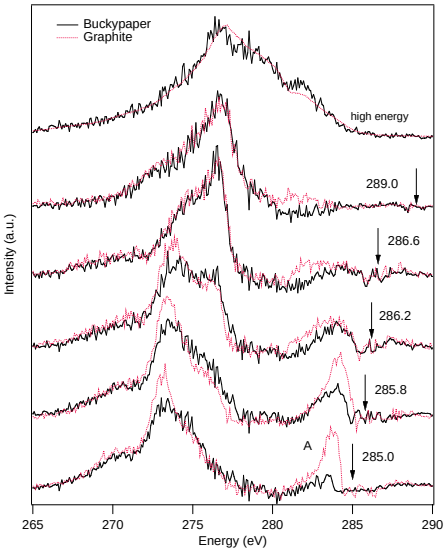

Fig. 5: (right) Resonant inelastic soft x-ray scattering spectra of single wall carbon nanotubes (solid line) and non-oriented graphite (dotted line). The excitation energies in eV are indicated at the respective spectra. The high energy excited spectra were obtained with 400 eV photon excitation (SWNTs) and 3 keV electron beam excitation (graphite). The incoherent contributions to the raw data have been subtracted, as well as a Voigt curve to account for the diffuse reflection/ recombination (arrows). Features A and B arise due to states at the *K*-point in the BZ.

The different spectral features in the graphite RIXS have been assigned by Carlisle *et al.* [11] in a **k**-conservation framework in the single electron approximation. While the validity of the single electron approximation has been questioned by van Veenendaal and Carra [12], these excitonic effects do hardly affect the very lowest and very highest states at the *K*-point (labeled $P_{3,1}^{+}$ and P_{3}^{-} in Fig. 1. As pointed out above, the states at the *K*-point are of particular interest for the electronic structure of SWNTs.

In the graphite RIXS spectrum excited at 285.0 eV, the broad emission feature at 270 eV emission energy labeled *B* is due to emission from the lowest two occupied bands at the *K*-point, corresponding to states around 13 eV below E_F in the bandstructure reproduced in Fig. 1. These states can be unambiguously assigned, as they are the only states in this binding energy range within the whole BZ. Preferential emission from the *K*-point is expected for this choice of excitation energy just at the absorption threshold (Fig. 4), as the core electron is promoted into the first available unoccupied states, which are at the *K*-point (see Fig. 1).

For the SWNT sample excited at 285.0 eV, we observe an emission feature of the same shape and at the same emission energy as in graphite. For the same reasons as in graphite, we assign this feature to emission from low energy states at the *K*-point. This is consistent with threshold excitation into the lowest unoccupied states, as those are always derived from states in the immediate vicinity of the *K*-point, as outlined above. We would like to point out that RIXS with threshold excitation probes selectively those SWNTs within the buckypaper which have their lowest unoccupied states as low in energy as possible, i.e. at E_F. Due to the finite width of the radiation used for excitation (0.4 eV) and the C 1s core level involved in the absorption transition (0.09 eV), we can not distinguish metallic and narrow-gap SWNTs, but wide gap SWNTs are easily discriminated against.

We now turn our attention to the highest energy RIXS feature labeled *A* in Fig. 5. This feature is located around 284.1 eV emission energy. For the spectra recorded using an excitation energy of 285.0 eV, this spectral feature is in the immediate vicinity of the intense peak due to diffuse reflection (subtracted at position of arrow, see Ref. [7]). For graphite, this feature has been assigned to emission from the highest occupied states, located at the *K*-point. For the SWNTs, we observe intensity in the RIXS spectrum at the same energy. For the same **k**-conservation reasons as in graphite, this feature can unambiguously be assigned to emission from states at the *K*-point. We can therefore directly observe those occupied states at E_F which are

degenerate (or quasi-degenerate) with the unoccupied states at *K* and which are responsible for the high room temperature conductivity of SWNTs with suitable *(n, m)*.

Emission from these states can be seen more clearly in the RIXS spectra when the excitation energy is increased to 285.5 eV, as the intense elastic peak is then further separated in energy. Comparing the spectra from the SWNTs and the graphite, we see that the emission feature is clearly visible in the SWNTs spectrum, but it is less intense than in graphite. This difference in intensity is due to the fact that at this energy, wide gap nanotubes can be excited as well. These nanotubes do not contribute to the high energy emission feature, as they have no occupied states close to E_F. When the excitation energy is further increased, more states within the BZ are probed according to the dispersion of the unoccupied bands. As a result, the spectra are not specific for the *K*-point anymore.

In conclusion, we have studied the electronic structure of SWNTs in "buckypaper". Using threshold excitation, we have selectively investigated SWNTs with *unoccupied* states in the immediate vicinity of E_F. Our RIXS studies show that these states correspond to states in the close neighborhood of the *K*-point in graphite. For these SWNTs, we find *occupied* states at or close to E_F at the *K*-point as well, in agreement with predictions from bandstructure calculations. These (quasi-)degenerate states are responsible for the good room temperature conductivity of metallic and narrow-gap SWNTs.

While we can directly access those states by RIXS spectroscopy, a quantitative determination of the amount of metallic tubes in the sample is not possible, as pure reference samples with just one *(n, m)* SWNT do not exist. However, a follow-up scanning tunelling spectroscopy study [8] on the same buckypaper sample shows the fraction of metallic SWNTs in the sample to be 34 ± 6%, which is in qualitative agreement with our RIXS data.

ACKNOWLEDGMENTS

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